Report for 2005NJ89B: Impacts of Organic Matter Heterogeneity on Desorption and Availability of Sediment-bound PCBs

Publications

- Other Publications:
    - Ma, Yingjun; Song, Jianzhong; Xiao, Baohua; Totten, Lisa A.; Huang, Weilin (2006) Carbonaceous materials in sediments and their role in the equilibrium sorption of phenanthrene by sediments. (in preparation)
- unclassified:
    - Ma, Yingjun; Xiao, Baohua; Totten, Lisa A.; Huang, Weilin (2006) Quantification of exchangeable phenanthrene bound on soils and sediments with isotope-labeled compounds. (in preparation)

Report Follows

Problem and Research Objectives

Anthropogenic organic chemicals typically bind to suspended particulate matter and colloids, facilitating their transport via surface runoff or advective flow and allowing them to accumulate in estuarine sediments. These sediment-bound contaminants can later be released to the water column via resuspension and desorption, becoming available to living organisms and posing serious risks to the ecosystem. Although some severely contaminated coastal and estuary sites may be partially restored by dredging, containment or other remediation schemes, PAH/PCB residues in many estuaries remain uncontrolled due to high cost of clean-up procedures, becoming potential long-term threats for exposure. A detailed scientific understanding of mobility, reactivity and availability of these contaminants is critical to predicting fate of contaminants and their effects on organisms and ecosystems and to assessing related environmental risks in uncontrolled coastal and estuary environments. This scenario is occurring in the Hudson River/New York-New Jersey Harbor Estuary. PCBs released into the Upper Hudson River and stored in the riverine sediments are being transported into the New York-New Jersey Harbor Estuary, where they have the potential to accumulate in the estuarine sediments and/or to desorb from the particulate matter, rendering them bioavailable to the estuarine food chain. The Upper Hudson contributes about half of the entire PCB load to the New York-New Jersey Harbor Estuary (TAMS Consultants et al., 1997; Farley et al., 1999; Totten, 2004). Thus desorption of PCBs from Upper Hudson sediments has the potential to be the single most important mechanism for releasing PCBs in to the food chain of the estuary. Alternatively, Yan (2003) demonstrated that phytoplankton in Raritan Bay display PCB congener patterns similar to those found in the atmosphere, and argue, based on kinetic modeling of air-water exchange and uptake by phytoplankton, that the atmosphere is the single most important source of bioavailable PCBs in the system. This research will determine whether desorption of PCBs from contaminated sediments is fast enough to compete with air-water exchange as an important process controlling the bioavailability of PCBs in the estuary. The answer to this question has important implications in the management of PCB contamination in the Estuary.

We proposed this study to characterize and quantify Humic Acid (HA), Black Carbon (BC) and kerogen in sediments and to investigate the role of each of the three Sediment Organic Matter (SOM) fractions in the sorption, desorption and bioavailability of PAHs/PCBs bound on sediments. Our major hypotheses were that the sediments in the Hudson River Estuary and NJ/NY Harbor contain both coaly material and black carbon and that particulate organic matter such as BC and coaly materials dominate the sorption, desorption and environmental availability of bound PAHs and PCBs. The specific objectives of this study were to:

1) fractionate, quantify, and characterize major SOM fractions for Hudson River sediments;

2) characterize the role of particulate organic matter in the sorption of PAHs and PCBs on Hudson River sediments;

3) quantify desorption of PAHs/PCBs from the sediments;

4) estimate the availability of sediment-bound PAHs/PCBs to environmental acceptors.

Methodology

Fractionation and characterization of SOM

We obtained seven Hudson River sediment samples from the Institute of Marine and Coastal Sciences at Rutgers. For comparison, we selected three additional sediments collected from the Delaware River, Baltimore Harbor, and the Anacostia River of Washington DC. These samples were characterized in terms of their contents of HA, BC, and kerogen following a procedure of Song et al. (2002). Briefly, each sediment sample was extracted with NaOH following a standard base extraction procedure (Hayes, 1985) to obtain humic acid (HA). The HA was recovered from the extract and the solid residue was demineralized using an HCl (6 *M*) + HF (22 *M*) acid mixture at 60°C for 20 hrs. After digestion, the content was centrifuged, the residue was rinsed with 2 *M* HCl and milli Q water and dried at 60°C. The solid residue contained both kerogen and BC, and was designated as KBC (kerogen + black carbon). The latter (BC) was isolated by treating the solid with a hot dichromate/sulfuric acid in which kerogen was oxidized while BC remains mostly unchanged.

The isolated HA, KBC, and BC were freeze-dried, weighted, and stored in glass bottles for use in characterization. The total organic carbon (TOC) contents of the SOM fractions were analyzed with a high temperature combustion method. The ash contents were determined independently by complete oxidation of each SOM fraction under 950°C in a furnace. The organic facies and the shapes, sizes, and degree of maturation of the BC and KBC fractions were examined under an optical microscopy in transmitted and reflected mode.

Sorption experiments

All ten sediment samples were used in this study as the sorbents. To examine the role of BC and kerogen in the sorption of PAHs and PCBs, the 10 samples were Soxhlet extracted with dichloromethane to remove any existing PAH/PCB residues, and the extracted sediments were used as sorbents for sorption studies.

Phenanthrene and two PCB congeners (3,4,6'-trichlorobiphenyl (IUPAC #35) as a planar congener and 2,2',6,6'-tetrachlorobiphenyl (IUPAC #54) as a non-planar congener) were chosen as the Hydrophobic Organic Chemical (HOC) probes in this study. The aqueous solution used in the sorption equilibrium experiments contained 0.005 M $CaCl_2$ to simulate the electrolytes present in natural water and 100 mg/L of NaN_3 as a microbial inhibitor. The pH of the solution was adjusted and maintained at 7.0 ± 0.2 with $NaHCO_3$. A primary solute stock solution was prepared by dissolving an appropriate amount of

each chemical in HPLC-grade methanol. Methanol stock solutions of various solute concentrations were obtained by sequential dilution from the primary solution. Initial aqueous solutions with different solute concentrations were prepared by mixing desired volumes of the appropriate stock solution with the aqueous solution and were used for sorption experiments. All aqueous solutions used for sorption experiments contained < 0.2% of methanol.

Sorption equilibrium experiments were conducted at 22 ^{o}C using flame-sealed glass ampules (10 mL, Kimble) as batch reactor systems. The experimental procedures detailed in Huang et al. (1998) and Xiao et al. (2004) were exactly followed. Preliminary tests were run to determine an appropriate solid-to-solution ratio for each sorbent-sorbate system to achieve 40-60% reduction of the initial aqueous phase concentrations. Sorption rate tests were performed, and the results showed that a solid-solution contact time of 21 d was sufficient for attainment of apparent sorption equilibrium for all sorbent-solute systems.

The final tests were conducted with the same procedure as the preliminary tests for collecting the sorption data reported here. In each test, ampules containing a predetermined amount of sorbent and an appropriate amount of aqueous solution, with a headspace of about 0.8 mL, were flame-sealed in a natural gas flame. After being checked for leakage and shaken by hand for initial mixing of the contents, the sealed ampules were placed on a shaker set a speed of 125 rpm for mixing. After shaking for 21 d, the ampules were set upright for 2 d to allow solids to settle, then were flame opened. Immediately an aliquot of ~3 mL of the clear supernatant was carefully withdrawn from each reactor without disturbing the settled solid phase, and mixed with ~2 mL of HPLC grade methanol in a pre-prepared 5-mL glass vial. The amounts of methanol and supernatant were weighed on a balance, and a dilution factor was calculated based on mass ratio and the density data of the mixture. The supernatant-methanol mixtures were used for analysis of solute concentrations in the equilibrated solution phase with an HPLC method described below.

Control experiments were conducted using reactors containing no sorbent for assessing loss of solutes to reactor components during sorption tests. Results showed that average system losses were consistently less than 4% of initial concentrations of sorbate; hence, no correction was made during reduction of sorption data.

Solute concentrations in the initial and the equilibrated supernatants were measured with a reverse-phase HPLC (ODS, 5 μm, 2.1 $\times$ 250 mm column on a Hewlett-Packard model 1100) with both diode array UV detector at a detection wavelength of 250 nm and fluorescence detector (model HP 1046A, UC excitation/emission wavelengths at 250/332 nm for phenanthrene). External standards in methanol of each solute were used to establish linear calibration curves for both detectors. Each aqueous-phase solute concentration was calculated from the solute concentration in its respective aqueous methanol mixture determined from HPLC and the dilution factor. The solid-phase sorbate concentrations (q_e) at equilibrium condition were computed on the basis of mass balance between the two phases.

Desorption Equilibrium

We have developed an exchange method for measuring desorption of organic pollutants bound on sediments. Briefly, the equilibrium sorption of non-labeled phenanthrene was attained for reactor systems described above. The ampules were flame-opened and an aliquot of supernatant was transferred out for analysis of phenanthrene distribution between the water and the sediment phase. The reactor was then spiked with ^{14}C-labelled phenanthrene. The reactor was then flame-sealed and equilibrated for 21 d. After requilibration, the reactor was opened for analysis of both ^{14}C-labelled phenanthrene and the total phenanthrene concentrations in the supernatant. Through accurate mass balance calculation, the exchangeable fraction of sediment-bound non-labeled phenanthrene can be quantified at different concentrations of the phenanthrene. Similarly, an array of reactors with ^{14}C-labelled phenanthrene as the starting solute were initiated, and the non-labeled phenanthrene was introduced as the solute for displacing ^{14}C-labeled phenanthrene that had been bound on sediments. In addition to these two sets of experiments, two types of control reactors with non-labeled phenanthrene were run for 21 days and 42 days, respectively, to trace the effect of slow sorption rate on the observed difference in the measured sorption equilibria with respect to exchangeable versus non-exchangeable fraction of phenanthrene bound on the sediments.

The data collected using this method are still being processed. It is expected that the exchangeable fraction of the phenanthrene bound on sediments could be bioavailable whereas the non-exchangeable fraction could be less bioavailable or could not be accessed at all by microorganisms in the aquatic environment.

Principal Findings and Significance

Black Carbon in Hudson River Sediments

The major finding of this study with respect to the characterization of sediment organic matter is that kerogen and BC particles are the major organic components in the river sediments. The quantitative results are summarized in Table 1, which indicates that HA is less than 25% of the total organic carbon, and BC is about 25%. Other organic matter such coaly particles constitute approximately half of the organic matter.

KB particles were identified based on the characteristics observed under the petrographic microscope in transmitting and reflecting modes. Major representative organic facies are shown in the Figures 1 and 2. Generally, kerogen and BC of SOM have a spectrum of features under the microscope, depending upon their origins, types of macerals, and maturation. Under the reflecting microscope (Figure 1), more matured and condensed BC (fusinite and semifusinite) particles are brighter and hence have higher reflectance. Kerogen (i.e., vitrinite), a major maceral of coal materials derived diagenetically from plant or humus materials, is identified in the KB fractions with characteristics of gray color, relatively low reflectance indices, and smooth and

homogeneous surfaces (Figure 1 (a)-(d)).   Fusinite and semifusinite, having unique burning and charring properties, are identified in KB and BC fraction.   Compared to vitrinite, fusinite was characterized by its brightness, irregular dark-colored pores, spherical structures (Figure 1 (a), (e), (h)) and irregular shapes (Figure 1 (c), (d), (f), and (h)).   Semifusinite was found in smaller quantities having yellow color and smooth surfaces (Figure 1 (f)).   Under the transmitting microscope (Figure 2), the transparency of an SOM particle is inversely related to its maturation or condensation.   Less matured kerogen is semitransparent, whereas highly matured BC particles are opaque with spherical (Figure 2-(e)), elongate (Figure 2-(f)) and irregular shapes.

Sorption isotherms

All sets of equilibrium sorption data collected in this study were fitted to one of the Freundlich equations shown below.

$$q_e = K_F C_e{}^n \tag{1}$$

$$\log q_e = \log K_F + n \log C_e \tag{2}$$

where q_e and C_e are the equilibrium solid-phase and aqueous-phase solute concentrations expressed as µg/kg and µg/L, respectively; K_F $((µg/kg)/(µg/L)^n)$ and n are the Freundlich model capacity parameter and the isotherm nonlinearity index, respectively.   A linear regression procedure with SigmaPlot software (Version 9.0) was used for fitting Eq. 1 to the logarithmically transformed sorption data collected for each sorbent-sorbate system. The resulting model parameters, along with standard errors in the estimation of the parameters, and the R^2 values, are listed in Table 2.   The K_{oc} $(= (q_e/C_e)/f_{oc})$ values of phenanthrene were calculated at four different C_e levels ($C_e/S_w = 0.001, 0.01, 0.1$, and $C_e = 10$ ng/L) from their respective Freundlich model parameters.   The results are also presented in Table 2.   The sorption isotherms are shown in Figures 3 and 4.

The sorption data for the two PCB congeners have not been analyzed yet, which will be available within 3 months.

Isotherm nonlinearity and sorption capacity

The data presented in Table 2 and Figures 3 and 4 show that the sorption isotherms of the original Hudson River sediments for phenanthrene are nonlinear, with the n values ranging from 0.840 to 0.962. Comparatively, the sorption isotherms of the other three rivers are generally more linear than those of the Hudson River, ranging from 0.934 to 0.991.   The sediments Soxhlet-extracted with DCM exhibited much more nonlinear sorption equilibria than do the original sediments, with the n values ranging from 0.667 to 0.792 for the Hudson River sediments and from 0.728 to 0.814 for other river sediments. A possible explanation for this change is that the original sediments may contain simple organic chemicals such as fatty acids and organic pollutants such as chlorinated pesticides, PCBs and PAHs (Tabak et al., 2003). The preloaded organic molecules may have preferentially occupied the high energy "sites" that exhibit more nonlinear sorption. The unoccupied "sites" may exhibit relatively more linear sorption so

that the overall sorption isotherms measured for the target sorbates are more linear due to the competitive effect (Xiao et al., 2004).

These preexisting simple chemicals in the original sediments may have also decreased the sorption capacity for the target solutes. Removal of the chemicals by Soxhlet extraction could increase both the capacity and nonlinearity of the sorption isotherms for phenanthrene. This competitive effect is more prominent when total q_e is far less than the saturation limit, or C_e is in low concentration ranges. The data in Table 2 indicate that, due to variations in TOC contents and n values, the log K_F values vary from 2.997 to 3.375. Compared to their respective original sediments, Soxhlet extracted sediments exhibit log K_F values approximately twice as high as their original samples. As mentioned above, this is likely due to the preoccupation of the high energy "sites" by the preexisting organic molecules.

The calculated K_{OC} values exhibit much less variation since the effect of TOC content was eliminated (Table 2). From the calculated results of single-point log K_{OC} (Table 2), we can find that (i) the K_{OC} value decreases as a function of C_e, indicating the effect of isotherm nonlinearity; (ii) at lower C_e levels, the original sediments exhibit much lower sorption capacities than their respective Soxhlet extracted samples; (iii) at C_e = 10 ng/L, which is approximately the concentration of phenanthrene in natural waters, the K_{OC} values of Soxhlet extracted sediments are approximately 5~6 times of their respective original sediments, which means that under natural water conditions sorption capacity of actual river sediments for phenanthrene is much lower than that of "clean" or organic solvent extracted ones.

This study demonstrated that black carbon and coaly materials are dominant sediment organic matter in the samples tested and that the untreated sediments exhibited more linear sorption isotherms with lower K_D values at low concentrations. After extracted with organic solvents, the sediments samples displayed much more nonlinear isotherms for phenanthrene with larger sorption capacities. These observations suggested that the role of black carbon and coaly materials in the equilibrium sorption of PAHs may be dramatically diminished after aging of the carbonaceous materials in the sediments. This finding challenges the predictive means developed for quantitatively assessing the equilibrium sorption and desorption of organic pollutants from single measurements of the black carbon content in the sediments. Direct measurement of sorption equilibria with a representative organic pollutant probe is likely required for predicting contaminant distribution in environmental media.

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TABLE 1. Sediment Properties

Sediments	Source	TOC (wt %)	HA (%)	KBC (%)	BC (%)	Site description
HR	Hudson River	5.68	23.0	56.1	28.0	Date: 10/25/2004 Location: Berry's Creek (a tributary of the Hackensack river)
HR1	Hudson River	7.09	0.89	93.0	72.4	Date: 04/29/2004 Location: 40 43.297N, 74 01.680W, 2.6 km from battery
HR2	Hudson River	2.35	6.79	59.7	24.6	Date: 04/29/2004 Location:40 53.287N, 73 56.152W, 19.7 km from battery
HR12	Hudson River	2.14	11.4	58.4	26.7	Date: 04/29/2004 Location:25.4km from battery
HR13	Hudson River	2.29	23.2	52.6	23.0	Date: 04/29/2004 Location:41 01.020N, 73 53.430W, 33.9 km from battery
HR15	Hudson River	1.92	14.8	65.4	18.2	Date: 04/29/2004 Location:41 03.323N, 73 52.909W, 37.8 km from battery
HR17	Hudson River	2.31	3.58	61.6	26.6	Date: 04/29/2004 Location:40 49.181N, 73 58.322W, 12.6 km from battery
BH	Baltimore Harbor, MD	3.91	1.58	82.2	42.6	N/A
WR	Anacostia River, Washington DC	3.26	13.82	64.8	34.5	N/A
PP	Delaware River, Philadelphia	nd				Penn's Landing area, 2nd street

TABLE 2. Phenanthrene Sorption Isotherm Parameters

Sediment		n		$\log K_F$ [a]		R^2	Single-point $\log K_{OC}$ [b]			$C_e = 10$ ng/l
							$C_e/C_S=10^{-1}$ [c]	$C_e/C_S=10^{-2}$	$C_e/C_S=10^{-3}$	
HR	Before Extraction	0.962	0.027	3.375	0.050	0.986	4.543	4.581	4.619	4.697
	After Extraction	0.792	0.017	3.752	0.031	0.992	4.571	4.779	4.987	5.414
HR1	Before Extraction	0.937	0.026	2.997	0.049	0.986	4.017	4.080	4.143	4.272
	After Extraction	0.673	0.017	3.755	0.029	0.989	4.234	4.561	4.888	5.558
HR2	Before Extraction	0.844	0.017	3.168	0.032	0.992	4.477	4.633	4.789	5.109
	After Extraction	0.707	0.012	3.547	0.023	0.995	4.576	4.869	5.162	5.762
HR12	Before Extraction	0.843	0.011	3.158	0.020	0.997	4.506	4.663	4.820	5.142
	After Extraction	0.705	0.012	3.548	0.022	0.995	4.613	4.908	5.203	5.808
HR13	Before Extraction	0.855	0.014	3.119	0.025	0.995	4.462	4.607	4.752	5.049
	After Extraction	0.667	0.012	3.613	0.021	0.995	4.571	4.904	5.237	5.919
HR15	Before Extraction	0.840	0.013	3.062	0.024	0.996	4.451	4.611	4.771	5.099
	After Extraction	0.675	0.019	3.500	0.035	0.986	4.551	4.876	5.201	5.867
HR17	Before Extraction	0.849	0.011	3.144	0.020	0.997	4.471	4.622	4.773	5.082
	After Extraction	0.707	0.014	3.508	0.026	0.993	4.544	4.837	5.130	5.730
BH	Before Extraction	0.934	0.009	3.467	0.016	0.998	4.740	4.806	4.872	5.007
	After Extraction	0.728	0.011	3.983	0.021	0.996	4.833	5.105	5.377	5.935
WR	Before Extraction	0.991	0.014	3.194	0.026	0.996	4.662	4.671	4.680	4.699
	After Extraction	0.814	0.015	3.595	0.028	0.994	4.701	4.887	5.073	5.454
PP	Before Extraction	0.940	0.019	3.195	0.036	0.992	nd [d]	nd	nd	Nd
	After Extraction	0.767	0.011	3.611	0.020	0.997	nd	nd	nd	nd

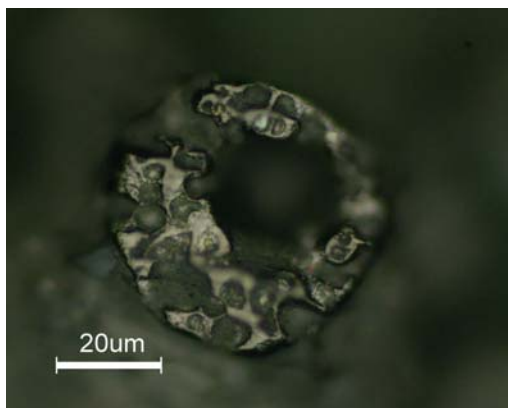[a] Freundlich isotherm coefficient with units of $((\mu g/kg)/(\mu g/L)^n)$
[b] organic carbon normalized distribution coefficient at a given aqueous phase concentration, with units of L/kg.
[c] C_e and C_S are aqueous phase phenanthrene concentration and aqueous phase phenanthrene solubility limit, respectively. $C_S = 1.12$ mg/l at 20°C.
[b] nd, not calculated.

Figure 1. Microphotographs of the isolated SOM particles under the microscope of reflecting white light mode.

(a) KB (HR2)

(b) KB (HR1)